Metals Leaching from Cenospheres using Batch Tests with Varying pH

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Background

Subsequent to the Kingston Ash Event on December 22, 2008, large areas of floating cenospheres (fly ash coalesced around entrained bubbles) drifted downstream and were of concern to the surrounding community. TVA studied these using EPA Proposed Method 1313.

Test Results

Cenospheres were collected by flotation from freshly produced ash from the TVA Johnsonville Fossil Plant in New Johnsonville, TN and transported to the TVA laboratory facilities in Muscle Shoals, AL. Samples were air-dried at room temperature to a moisture content of 7.51% (g water/g dry weight of material) before use.

Fly ash was also collected from the Kingston ash spill area for comparison to the cenospheres.

Samples were prepared in accordance with Method 1313, using pre-test titration runs to determine the amounts of acid and base additions required to obtain target pH levels of 2, 4, 5.5, 7, 8, 9, 10.5, 12, and 13 (±0.5 around the target value). For each sample, water containing trace-metal grade nitric acid or ACS grade potassium hydroxide was added to 20 g of cenospheres (dry weight basis) for a final volume of 200 ml (liquid:solid ratio of 10:1). Two replicates of each target pH were run. Samples were tumbled end-over-end at 28±2 rpm for 24 hours. After tumbling, the liquid and solid phases were settled for approximately 30 minutes, filtered through a 0.45 micron filter, and analyzed at TestAmerica Nashville using the EPA SW-846 analytical methods.

Arsenic results (Figure 1) display an amphoteric response, with greater leaching in the acidic range, minimum leaching in the neutral and slightly acidic pH values, and greater leaching at alkaline pH. Antimony, although not presented here, also showed this response. Aluminum, boron, copper, and vanadium also displayed amphoteric responses, but leaching at higher pH levels was only slightly greater than in the neutral range (e.g., Figure 2 for aluminum). The pH levels in the rivers affected by the Kingston Ash Event are in the neutral and near-neutral pH range, which is also the range of minimum leaching for the amphoteric-response elements. These results indicate minimal leaching of amphoteric elements from cenospheres will occur in these rivers.

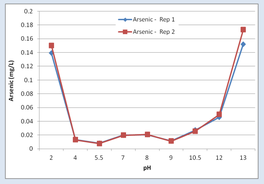

Figure 1. Results of Method 1313 Batch Leaching Test for Arsenic

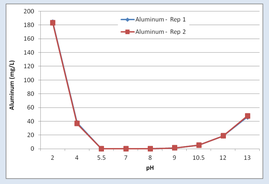

Figure 2. Results of Method 1313 Batch Leaching Test for Aluminum

Several metals (barium, cadmium, calcium, chromium, cobalt, magnesium, manganese, nickel, sodium, and strontium) exhibited the response of cationic species to leaching (e.g., Figure 3 for cadmium), with maximum concentrations in the acidic pH range, and decreasing with increasing pH.

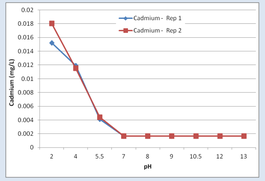

Figure 3. Results of Method 1313 Batch Leaching Test for Cadmium

Several others leached significantly only under highly acidic conditions. Beryllium and zinc had leaching only at pH 2 and 4, and iron, lead and thallium only had significant leaching at pH 2. Conversely, mercury was only leached at pH 13. No detectable silver leached from the cenospheres.

Selenium and molybdenum displayed leaching curves unlike the other analytes (Figures 4 and 5). These metals showed unusual cenosphere leaching curves in a previous study conducted at TestAmerica; this study was conducted in part to reassess selenium and molybdenum leaching. For this study, replicate results for each analyte matched very closely, and the leaching curves for selenium and molybdenum were very similar to each other.

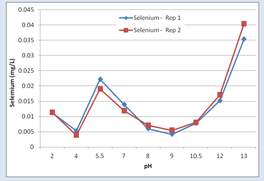

Figure 4. Results of Method 1313 Batch Leaching Test for Selenium

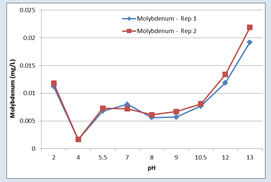

Figure 5. Results of Method 1313 Batch Leaching Test for Molybdenum

Leaching of arsenic and selenium from cenospheres were compared to results from leaching studies of fly ash samples from the Kingston fossil plant (Figures 6 and 7). "KIF Fly Ash" refers to an initial study using Kingston ash over a pH range of 5 to 11 (TVA 2010). "KIF Fly Ash-Suppl" was a subsequent study over a pH range of 5 to 13 (TVA 2011). Arsenic leaching for both the cenospheres and fly ash samples was lowest for pH 5 through 8, with concentrations for fly ash samples about 2 to 4 times greater than for cenospheres. At pH 9 and above, leached arsenic from fly ash increased to a maximum of 4.57 mg/L at pH 13 (Figure 6), while concentrations from cenosphere leaching increased relatively slightly to 0.173 mg/L at pH 13.

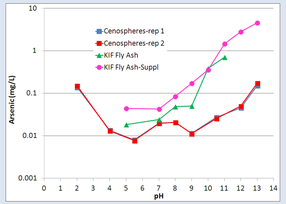

Figure 6. Arsenic Leaching from Cenospheres and Kingston Fly Ash

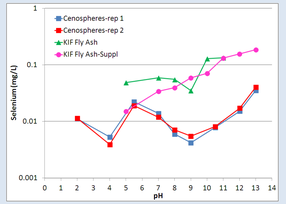

Figure 7. Selenium Leaching from Cenospheres and Kingston Fly Ash

Above about pH 5, selenium leaching from fly ash was higher than for cenospheres. The differences between fly ash and cenospheres continued to increase at higher pH values, particularly for KIF Fly Ash-Suppl (Figure 7). KIF Fly Ash leaching exhibited an apparently unusual pattern between pH 8 and 10.

Comparison to EPA's LeachXS™ Lite Data

The Vanderbilt University database, LeachXS™ Lite, which contains leaching results from coal combustion products, was used to obtain leaching rates from fly ash similar to that produced at another TVA Fossil Plant: Johnsonville. Prior to about 2000, all coal burned at Johnsonville was eastern bituminous coal with medium to high sulfur content from the Illinois basin. Over the last decade, the fuel was switched to predominately Powder River Basin coal mixed with Uinta basin coal (western bituminous low sulfur) and a small percentage of Illinois basin coal. In Figures 8 and 9, PRB/Bitum. (85/15) is used to represent fly ash currently produced at Johnsonville, and Bitum. medium S and Bitum. high S indicate Illinois basin coal fly ash. Values presented are averages of leaching rate results from a number of samples of each coal type.

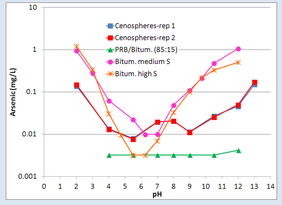

Figure 8. Arsenic Leaching from Cenospheres and Fly Ash

Arsenic leaching for bituminous fly ash with both medium and high sulfur showed an amphoteric response to pH (Figure 8), similar to that discussed above for cenosphere leaching (Figure 1), with minimal leaching in the neutral pH range around pH 7. Arsenic leaching for those fly ashes was much higher than for cenospheres in the low and high pH ranges. Arsenic leaching from the PRB/Bitum. (85:15) fly ash was below the method detection limit (MDL) of 0.0064 mg/L, and this was less than any of the cenosphere leaching rates. Arsenic leaching values from LeachXS™ Lite for PRB ash alone were also below the 0.0064 mg/L MDL (data not shown). This indicates that addition of PRB coal to the mixture being burned reduces arsenic leaching from the fly ash.

For selenium, leaching from the medium and high sulfur coal ashes was minimal in the pH range from 4 to 7. As with arsenic, leaching from the PRB/Bitum.(85:15) ash was relatively unchanged throughout the pH range. Leaching from the cenospheres varied slightly with pH, with concentrations approximately an order of magnitude lower than for the fly ashes (Figure 9). This indicates that cenospheres contribute minimally to selenium leaching from fly ash. Leaching increased for Bitum. medium S and Bitum. high S at the low and high pH levels, with leachate exceeding the 1.000 mg/L TCLP limit for selenium at pH 9 for Bitum. high S and at pH 12 for Bitum. medium S fly ash. Selenium in leachate from cenospheres and PRB/Bitum (85:15) fly ash was well below the TCLP limit.

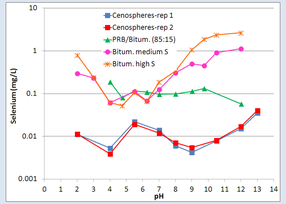

Figure 9. Selenium Leaching from Cenospheres and Fly Ash

The similarity in leaching patterns for cenospheres and PRB/Bitum (85:15) for arsenic and selenium suggests that the cenospheres tested may have been from coal burned within the last decade, as opposed to the medium and high S bituminous coals burned previously at the Johnsonville Fossil plant. If the cenospheres were representative of the previously-burned coal, they would have been expected to have exhibit leaching patterns and concentrations more similar to the fly ash.

Conclusions

This study shows that metals leach from cenospheres primarily at low and high pH extremes, with minimal leaching at neutral and slightly acidic or slightly basic pH values. Leaching from amphoteric metal species was minimal between pH 5.5 and 10.5. For cationic species, leaching rates declined at pH >5.5, with little or no leaching at pH 7 or higher. These results indicate that minimal leaching would occur from cenospheres in a neutral or near-neutral pH environment, such as the river system at the Kingston fossil plant.

For arsenic the highest cenosphere leaching concentration of 0.173 mg/L (at pH 13) was well below the TCLP limit of 5.0 mg/L; for selenium the highest concentration of 0.0403 (also at pH 13) was well below the 1.0 mg/L TCLP limit. The TCLP test, the USEPA regulatory leaching procedure for characterizing hazardous waste, differs from Method 1313 in that testing is conducted using an acetic acid buffer at pH 2.88 or 4.93, a liquid:solid ratio of 20:1, and a leaching time of 18 hours.

This study of arsenic and selenium leaching from cenospheres and fly ash show that leaching characteristics vary significantly among coal sources, and that cenospheres contribute minimally to the overall amounts leached.

References

TVA 2010. December 2, 2010 (EPA approval). *Kingston Ash Recovery Project Non-Time –Critical Removal Action for the River System, Ash Leaching Test Results.* Document No. RAWP-072A. Prepared by Jacobs Engineering Group Inc.

TVA 2011. July 26, 2011 (EPA approval). *Kingston Ash Recovery Project Non-Time –Critical Removal Action for the River System, Supplemental Ash Leaching Test Results for Stabilized Ash.* Document No. RAWP-072B. Prepared by Jacobs Engineering Group Inc.